

Orbital order in NaTiO₂ : A first principles study

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(Dated: September 8, 2011)

The debate over the orbital order in layered triangular lattice system NaTiO₂ has been rekindled by the recent experiments of McQueen, et al.¹ on NaVO₂ (*Phys. Rev. Lett.* **101**, 166402 (2008)). In view of this, the nature of orbital ordering, in both high and low temperature states, is studied using an ab-initio electronic structure calculation. The orbital order observed in our calculations in the low temperature structure of NaTiO₂ is consistent with the predictions of McQueen, et. al. An LDA plus dynamical mean-field calculation shows considerable transfer of spectral weight from the Fermi level but no metal- insulator transition, confirming the poor metallic behaviour observed in transport measurements.

PACS numbers: 71.20.-b, 71.15.Mb, 75.25.Dk

Transition metal ions sitting at the vertices of triangles in a layered triangular lattice system present a very interesting playground for the study of competing interactions²⁻⁴. The presence of unfilled d-levels in the transition metal ion brings in correlations while the geometric frustration of the underlying lattice tends to prevent long range antiferromagnetic (AF) order. Consequent large entropy in the ground state usually relieves itself via broken symmetry at lower temperatures^{1,5}. If the transition metal ion is Jahn-Teller active, it is likely to induce frozen lattice distortions. It has been observed that orbitals often play an active role in removing the frustration leading to an orbitally ordered (OO) ground state^{1,6}.

The ongoing debate⁶⁻⁸ about the role of orbitals in quenching the spin requires more careful and diverse work. There is only a limited experimental and theoretical work available in the literature on NaTiO₂ to take a definitive call on this. It is already emphasized in earlier theoretical work^{6,7,9} that the spin degree is quenched via an orbitally induced Peierls transition at around 50K and the low temperature physics is dominated by the orbital correlations.

The absence of magnetic LRO, very small susceptibility below 250K, lack of Curie-Weiss behavior in any region of temperature, apparent Pauli paramagnetism above and below the broad transition region - virtually all experimental evidence so far, point towards a spin degree which is completely quenched at low temperature⁵. In addition, the entropy loss much in excess of $R \ln 2$ at the transition is a strong indication of the involvement of orbital degrees in the ordering process. While the transition is likely to be affected by spin fluctuations (getting quenched there - indicated by the drop in spin susceptibility), the role of spin degrees in selecting the ground state order is not clear. In fact most of the model calculations appear to support an orbitally driven symmetry breaking in the ground state.

There is a structural transition around 250K in NaTiO₂ with four short and two long Ti-O bonds per

octahedron in the low temperature phase⁵. Orbital order, concomitant with the structural transition, has been reported recently in NaVO₂¹ from high resolution XRD and powder neutron diffraction (PND). Both in structure and electronic configuration, NaTiO₂ is very similar to NaVO₂, where a transition driven by OO has been proposed earlier^{1,6,7}. However, it is not established yet what exactly is the nature of OO in the low temperature phase. Indeed, being a d^1 , $s = \frac{1}{2}$ system without a magnetic long range order (LRO), NaTiO₂ was hotly pursued originally as a candidate for spin liquid¹.

The structural transition that NaTiO₂ undergoes is from the high temperature rhombohedral phase (space group $R\bar{3}m$) to a monoclinic phase (space group $C2/m$) through a broad, continuous transition between the temperature range 220K to 250K⁵. In the rhombohedral phase Ti ions form 2D triangular planes separated by alternating Na and O planes (arranged as Na-O-Ti-O-Na... planes) along [111] direction. The interlayer Ti-Ti distance is much higher than intralayer Ti-Ti distance. It is therefore generally assumed that the interaction among the Ti ions of different layers is not relevant. Furthermore, the Ti ions are octahedrally coordinated by O ions and these TiO₆ octahedra share edges with each other. In the high temperature rhombohedral phase all six oxygens surrounding a Ti ion are equally distant and the Ti ions form isosceles triangles with all the Ti-Ti bonds being equal inside a layer. On cooling, it acquires a monoclinic structure where two among the six Ti-O bonds elongate and the remaining four shorten affecting Ti-Ti bonds as well: out of the six nearest neighbour intralayer Ti-Ti bonds, four are shortened and two elongated. This structural transition should evidently affect the electronic structure.

Previous electronic structure calculations⁷ within LDA+U approach predicted an insulating state for the high temperature rhombohedral phase. Whereas, experimentally, the system remains metallic, albeit with high resistivity, at all temperatures⁵. There are, however, no electronic structure calculation available in the literature

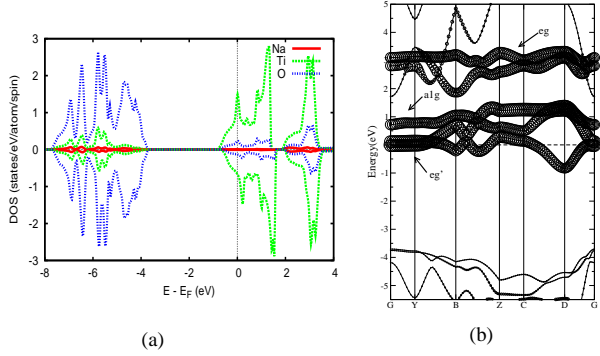


FIG. 1: (color online) Spin polarised density of states and LDA band structure (spin up only) of NaTiO₂ in the low temperature monoclinic phase. Bands are plotted in high symmetry directions and the d-orbitals are shown in the usual fat band scheme.

for the low temperature phase. In this context, therefore, a first principles calculation is quite pertinent. We investigate in detail the electronic structure of both high and low temperature phases from first principle calculations using linearized augmented plane wave (LAPW) method as implemented in the Wien2k code¹⁰.

We have taken the crystal structure and atomic positions from Clarke et al.⁵. In the high temperature rhombohedral phase, as already discussed, all Ti-O bonds in a TiO₆ octahedron are of same length, 2.08 Å, but there exists a trigonal distortion making O-Ti-O angles different from 90°. All intralayer Ti-Ti nearest neighbour bonds are of equal length as well, 3.04 Å. As discussed above, in the low temperature monoclinic structure two of the six Ti-O bonds in a TiO₆ octahedron are stretched to 2.11 Å while the remaining four Ti-O bonds become 2.05 Å each. However, the O-Ti-O bond angles get closer to 90° in this phase. Similarly six Ti-Ti bonds also divide into four short bonds (3.028 Å) and two long bonds (3.03 Å). So the Ti-Ti bonding increases in the low temperature phases which is reflected in the increase of conduction bandwidth by about 0.2 eV. Note that the distortion in Ti-O bonds is much higher than that of Ti-Ti bonds. In our LAPW calculation, the muffin tin sphere radii for Na, Ti and O were chosen to be 2.22, 2.05 and 1.82 a.u. respectively and approximately 200 *k*-points were used in the irreducible first Brillouin zone for the calculation.

We present in Fig.1 the density of states (DOS, in both spin directions) and the band structure (for spin up) in certain high symmetry directions for the low temperature monoclinic structure within local spin density approximation (LSDA). The *d*-bands are shown in the usual fat band scheme - where the width of the band represents the contribution of *d*-orbitals to the respective band, revealing the orbital contributions along different symmetry directions. The *e_g-t_{2g}* splitting due to the octahedral crystal field of oxygens is clearly visible. Presence of trigonal distortion, described above, further splits the *t_{2g}* levels into an *e'_g* doublet and an *a_{1g}* singlet. The shape

of *a_{1g}* singlet and *e'_g* doublet orbitals are shown in Fig. 2(a) and (b) respectively. The *e'_g* doublet is found to be lower in energy than the *a_{1g}* singlet, in contradiction to the predictions of crystal field theory as explained below.

This feature has been reported recently by Jia et. al¹¹ for the isostructural system NaVO₂ and has also appeared¹² in the study of Na_xCoO₂. The argument presented in all these cases is that there is a competition between crystal field effects and *e_g - e'_g* hybridization. Discussed at length by Landron and Lepatit¹³, it is the hybridization between *e'_g* and *e_g* orbitals (owing to their similar symmetries) which plays a dominant role in deciding the relative order of *a_{1g}* and *e'_g* orbitals which could often go against the crystal field theory predictions. These authors have shown from quantum chemical calculations in clusters, that interactions like metal-ligand hybridization, long range crystalline field effects, screening etc. have negligible effect in this regard. They have further shown that the value of the angle θ between three-fold (111) direction of the MO₆ octahedron and the M-O direction (schematically shown in Fig. 2(c) for TiO₆) plays a crucial role in dictating the energetics of *a_{1g}*, *e'_g* splitting. For a regular octahedron this angle is calculated to be 54.74 degrees¹³ while from the experimental structure data⁵ we estimate the angles to be 57.78° and 56.54° in the high and low temperature phases of NaTiO₂ respectively. So there is a (slight) compression along the (111) direction in comparison to the regular octahedron. This compression is also present in other isostructural systems such as NaVO₂, Na_xCoO₂. Under this trigonal compression, crystal field theory predicts *a_{1g}* orbital to be lower and *e'_g* orbitals to be higher in energy. However, we observe the opposite splitting like in the cases of NaVO₂ and Na_xCoO₂. Therefore, we believe that *e_g - e'_g* hybridization plays a dominant role in deciding the *t_{2g}* splitting in NaTiO₂ as well.

In the presence of transition metal ion Ti, with partially filled 3d-shell, the correlation effects are bound to be important. Furthermore, in order to ascertain the presence of any orbital order one needs to incorporate the Coulomb correlation as it stabilizes the order further. Therefore, we undertake an LSDA+*U* calculation and discuss our results below. From our calculations (with $U_{eff} = 3.6$ eV⁷) we observe that there is a clear splitting between *a_{1g}* and *e'_g* now (which was quite small in LSDA) and the relative order is indeed the same as in LSDA. We present the LSDA+*U* DOS (partial DOS for *d*-orbitals) and band structure (spin up direction only) in Fig. 3. It is also seen that on applying *U* all the down-spin weight of the *d*-states just below the Fermi level gets transferred to the spin-up sector leaving spin-down sector empty. The system appears to be half-metallic with 100% spin polarization at the Fermi level.

We have calculated the electron density at each Ti site to study if there is any orbital order and in case there is one, then the nature of the order in the low temperature phase of NaTiO₂. In Fig. 4(a) we show the real space electron density plot of the orbitals occupied by the sin-

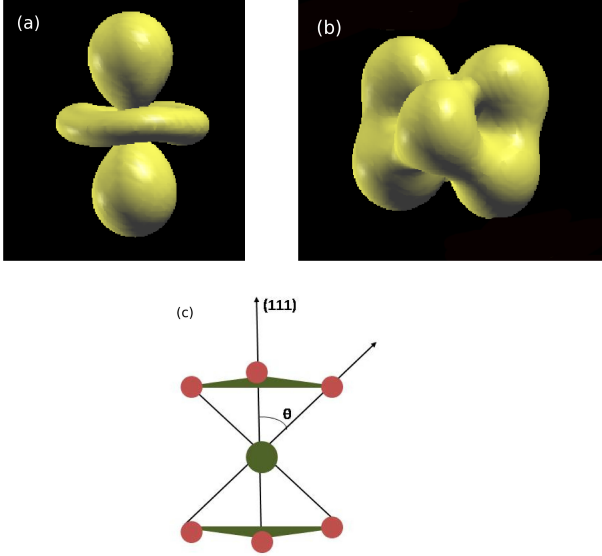


FIG. 2: (color online) Shape of (a) a_{1g} (singlet) and (b) e'_g (doublet) orbitals formed after the splitting of t_{2g} orbitals under the trigonal distortion. (c) The angle θ measuring trigonal compression of the octahedron.

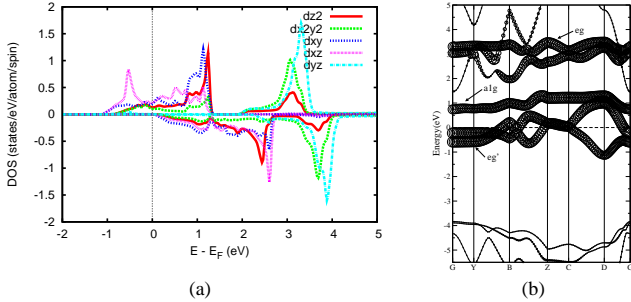


FIG. 3: (color online) Partial DOS for five d-orbitals around the Fermi level in both spin directions are shown in (a). Fermi level falls only in the spin up DOS. In (b) the bands are shown only for spin up direction in the fat band scheme highlighting the five d-bands.

gle d-electron at each Ti site. Comparing the electron density at each Ti site with that of Fig. 2(b) (where the shape of the e'_g doublet is shown), one can clearly see that both the e'_g orbitals are occupied by the single d-electron of Ti ion at each site. Note that in Fig. 2(b) the 3D orbitals are shown from one side whereas in Fig. 4(a) they are seen from the top with a slight tilt so they might look a bit different but they have the same 3D structure.

Looking at Fig. 4(a) more closely, it can also be seen that the lobes of the occupied e'_g -orbitals at each Ti site are oriented in such a way so as to have an anisotropy in the interactions (as explained below) with the six nearest neighbour Ti ions in the hexagonal plane. Along a particular direction (indicated here by thick lines) there would be comparatively more interaction among the neighbour-

ing Ti d-orbitals because lobes along this direction face each other more directly than along the other directions (shown by the thin lines). Orbital lobes facing each other along the thick line are indicated by curves with double ended arrows in Fig. 4(a) (with solid curves pointing at lobes which are above the hexagonal plane and dashed curves pointing at lobes which are below). Note that the lobes we are talking about here do not lie in the same hexagonal plane formed by the Ti ions, they lie in a plane which is nearly perpendicular (with a slight tilt) to the former. Therefore, the orbital overlap among the neighbouring Ti ions along this direction is not of “in-plane” σ -type, but it is “out of plane” π -type in which two lobes bind above the hexagonal plane and two lobes bind below. To make the above picture clearer we present in Fig. 4(b) a 2D intersection of the electron density in a plane (the red plane in Fig. 4(b)) which is nearly perpendicular to the hexagonal Ti plane. One can easily see that lobes of the xz -type orbitals at neighbouring Ti sites lie in the same plane (the red plane) along z -direction (thick lines in Fig. 4(a)) whereas they lie in planes parallel to each other along the y -direction. In this figure we have only shown 2D electron densities for some selected Ti ions for demonstration purposes.

From the above discussion it is clear that there exists some anisotropy in the interactions among nearest neighbour (nn) Ti ions along six different directions due to the directional nature of occupied orbitals at these sites. Among the six nn interactions, two (indicated by the thick lines in Fig. 4(a)) are more interacting than the other four (indicated by the thin lines in Fig. 4(a)). This is also reflected in the distortion of Ti-Ti bond distances observed experimentally in the low temperature phase as explained in the following. Due to the Coulomb repulsion being more along the two directions than the remaining four directions, the Ti-Ti bond distances are slightly higher (3.03 Å) than the remaining four Ti-Ti distance (3.028 Å). Thick lines in Fig. 4(a) correspond to higher bond distances and thin ones indicate lower bond distances.

Following the discussion above, one can infer that the occupied orbitals at Ti sites appear to form one dimensional orbital chains in the hexagonally arranged Ti plane. The thick lines in Fig. 4(a) indicate the orbital chain direction. Along the chain, a *ferro*-orbital order is observed with the lobes of the orbitals oriented in such a way (as shown above) so as to give rise to slightly stronger interaction among nearest neighbour Ti ions compared to that among the neighbouring chains. A schematic diagram with the orbital order proposed above is shown in Fig. 4(c) where the inplane projection on the hexagonal Ti-plane is shown. Note that the schematic Fig. 4(c) does not indicate sigma bonding along solid lines, it is a 2D projection from Fig. 4(a) that makes it appear so.

McQueen, et. al.¹ predicted a similar orbital order for NaTiO_2 using physical arguments, based on their experimental observations on NaVO_2 . This orbital ordering in the low temperature phase is a clear manifestation of the

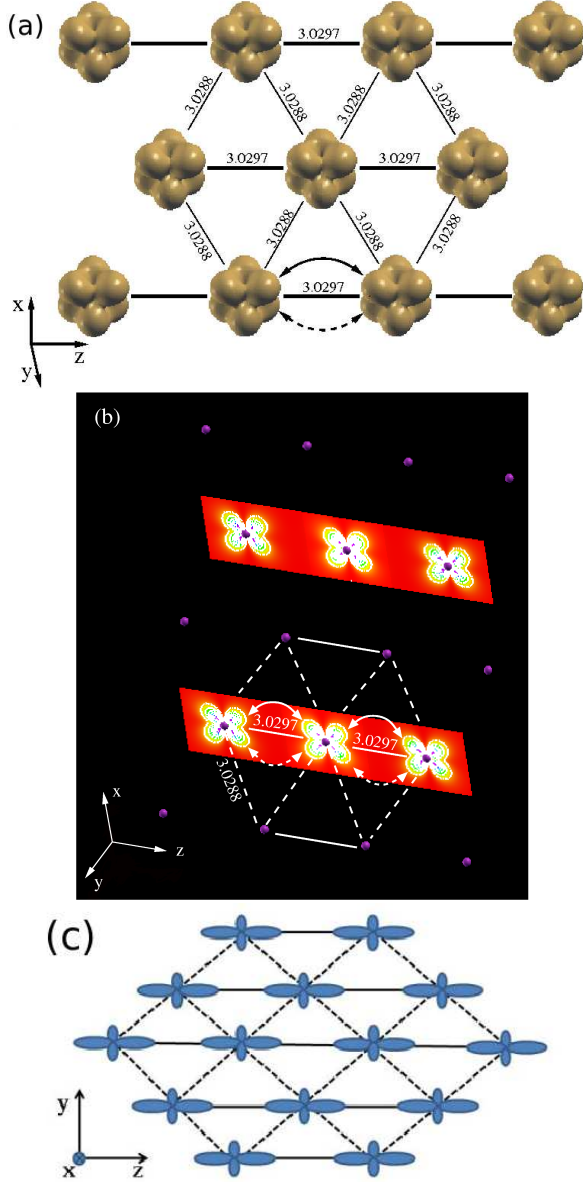


FIG. 4: (color online) (a) Electron density plot showing chain like orbital order in the hexagonal Ti plane (thick black lines indicate the orbital chain directions). Curved double ended arrows point towards the orbital lobes which participate in π type bonding along the orbital chains (see text), (b) 2D intersection of electron density in a plane (red plane) which is nearly perpendicular to the hexagonal plane formed by the Ti ions (small violet spheres indicate Ti ions). Dashed straight lines represent the shorter bonds and solid straight lines represent the longer bonds in the hexagon drawn. The two representative red planes shown are parallel to each other and each of them is nearly perpendicular to the hexagonal Ti plane. (c) Schematic view of the orbital order in the hexagonal plane formed by Ti ions as seen from the top. Dashed line represent the shorter bonds whereas the solid lines represent the longer bonds. Note that interaction along the solid lines (orbital chains) is of π -type and it is the plane projection of the orbital lobes from Fig. 4(a) that makes it appear like σ -type.

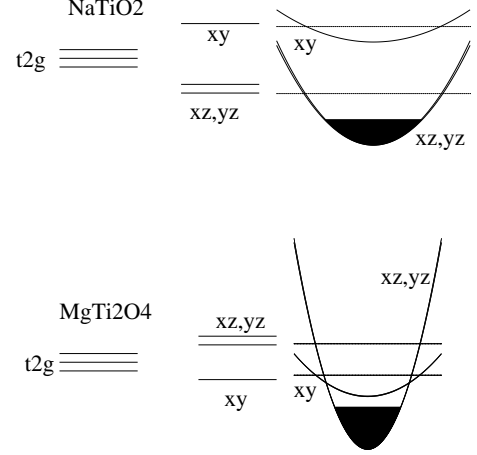


FIG. 5: (color online) Schematic diagram comparing the electronic structure of NaTiO_2 and MgTi_2O_4 in their low temperature phases. The parabolas on the right represent xy or xz/yz bands. The dashed lines show the reference positions of the centre of the band.

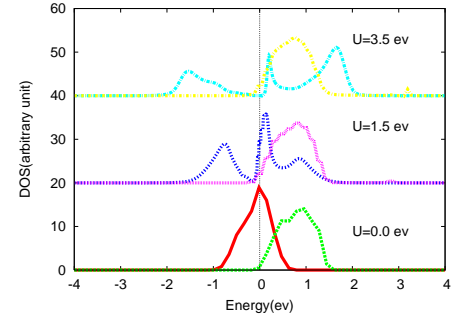


FIG. 6: (color online) LDA+DMFT DOS of the valence and conduction bands of NaTiO_2 in the low temperature phase for two different U values.

structural transition from rhombohedral to monoclinic which makes two out of the six Ti-O bonds in an octahedron unequal. So a reasonable distortion in the TiO_6 octahedra gives rise to a small but finite distortion in the inplane Ti-Ti bonding which in turn results in chainlike orbital order. This orbital order is found to remain stable in the range of U values varying from 2 to 7eV.

We have also looked at the electronic structure of the high temperature rhombohedral phase using LSDA and LSDA+ U methods. We do not observe any significant difference in the band structure from that of the low temperature phase. With LSDA+ U we get a half metallic state rather than an insulating state as observed by Ezhov et. al.⁷. Note that Clarke et al. predicted, from their experimental measurement, that there should not be any significant difference in the band structures across the structural transition. This is borne out in our DFT calculations too. Furthermore, their measurements also show that the system never becomes an insulator at any temperature, though the resistivity in the low temperature phase is fairly high, indicative of a “bad metal.”

The apparent similarity with the spinel MgTi_2O_4 prompted Khomskii and Mizokawa⁹ to speculate that the orbital order of NaTiO_2 is similar to MgTi_2O_4 . However, we find that in spite of their apparent similarity, there are certain important differences between the two systems. Due to the presence of strong trigonal distortion as well as tetragonal elongation, the t_{2g} band splits in the opposite way to that of MgTi_2O_4 as shown in the schematic picture comparing the electronic structures of the two in Fig. 5. Secondly due to the two dimensional nature of Ti-layer in NaTiO_2 the t_{2g} orbitals do not point towards each other (which would have given σ -bonding) and hence the overlap is not as strong as in the spinel MgTi_2O_4 . Therefore the bandwidths of the xy or xz/yz orbitals do not significantly increase due to the tetragonal distortion unlike in the case of spinels⁹. With dynamical shifting of spectral weight (see below) this band therefore remains more susceptible to the effects of strong Coulomb interaction, making the system a poor metal. Whereas, in case of MgTi_2O_4 , due to the significant increase in the band width, xy/yz doubly degenerate band extends below the singlet xy band and gets occupied by the Ti d-electron (see Fig. 5 (lower panel)).

Though the orbital polarization of both NaTiO_2 and MgTi_2O_4 in their low temperature phases looks similar from the band structure calculations (i.e. both xz and yz orbitals are being occupied), the orbital order we find in NaTiO_2 is different: there is no indication of the dimerization of orbitals (i.e., $yz - yz - zx - zx - yz - yz$). We rather find that both the orbitals are occupied at each site with their lobes oriented in such a way (as explained above) that one dimensional orbital chains are formed along a particular direction in the Ti plane. Over a physically reasonable range of U values (2-7 eV) we find this orbital order to remain stable and the system also remains metallic. Our observation of chain-like orbital order appears to be compatible with the scenario predicted in Ref¹ and Ref.⁶. Though this type of orbital order would prefer an antiferromagnetic exchange interaction among the ferro-orbital chains (according to Goodenough-Kanamori-Anderson rule¹⁴), the available neutron diffraction measurements⁵ do not indicate any long or short range magnetic order in this systems.

Although LDA+ U method gets qualitatively right broken symmetry ground states, it is well known that the spectral weight transfer (SWT) due to correlations is beyond such static approaches. They also overestimate the ‘gap’ in the DOS. Besides, the nature of the low temperature ‘bad metallic’ state is beyond the scope of LDA or LDA+ U calculations. The SWT is at the heart of the Mott physics and therefore we undertake an LDA plus multi-orbital dynamical mean-field theory (MO-DMFT) calculation using the two relevant bands (of e_g symmetry) close to the Fermi level. DMFT is exact in the infinite dimension and has been very successful in predicting the metal-insulator transitions and photoemission data in a host of correlated systems¹⁵. It captures the dynamical correlations quite well while mapping the problem onto

an impurity model. We use the iterated perturbation theory to solve the corresponding impurity model.

Shown in Fig. 6, with increasing intraband correlation U (taken the same for the two bands), are the gradual evolution of the DOS for the two bands. Two features are prominent here: (i) there is a gradual erosion of states at the Fermi level as U increases and (ii) SWT over a large range of energy that can be identified in photoemission spectroscopy. The erosion of DOS leads to a pseudogap like structure at the Fermi level consistent with the high resistivity observed. Even at a reasonably higher U , we do not observe a real gap opening at the Fermi level and the system remains nominally metallic. A clear signature of the building correlation is the appearance of the lower and upper “Hubbard bands” in the spectral density. The lower Hubbard band at around -1 to -2 eV can be easily picked up in a photoemission experiment confirming the correlated nature of the bands. We also note that the effect of an interband correlation is very small in the present case as the Fermi level is almost entirely in the lower band. Depending on the orbital characters of the two bands, this may indicate the possibility of preferential orbital occupation (“orbital selective” metallic state) and an orbital ordering. However, we do not see a Mott transition upto $U = 4.5\text{eV}$.

Finally, we sum up our findings from this first ab-initio calculation for the electronic structure and orbital order of the low temperature monoclinic phase of NaTiO_2 . As we have mentioned above, not much experimental or theoretical works are available to compare our results with. However, recent experimental measurements in the isostructural compound NaVO_2 ¹ have been used to make some predictions about the possible orbital order in NaTiO_2 . Our results appear to bear out their suggestions and are consistent with the possible order predicted thereof. Our LDA calculations reveal metallic states both above and below the structural transition which is consistent with the experimental observations as well. However, the metallic state found experimentally is a ‘bad metal’ while the LDA DOS at Fermi level is fairly high. We also find that the LDA+ U does not change this, though it stabilizes the orbital order further. This implies that the ‘bad metal’ state requires inclusion of dynamical fluctuations beyond single-particle description. Finally, incorporating dynamical corrections using LDA+DMFT calculations we show how large spectral weight transfer across the Fermi level leads to a bad metallic state as observed experimentally. We also observe that the orbital order of NaTiO_2 , speculated to be similar to that of MgTi_2O_4 (a Ti-spinel compound)⁹, has certain differences, though the orbital polarization is same in both the systems. The dimerization of orbitals forming singlet pairs, observed in MgTi_2O_4 , does not occur in NaTiO_2 .

In conclusion, we have studied the electronic structure of NaTiO_2 in both high temperature rhombohedral phase and low temperature monoclinic phase. We provide a theoretical resolution that the low symmetry state is, in fact, a poor metal and not an insulator. We also find

a considerable spectral weight transfer across the range and make predictions for the spectral densities that can be seen in photoemission experiments to establish the correlated nature of electronic states. Furthermore, in the low temperature phase, the system is found to be orbitally ordered with one dimensional chain-like order along a particular direction in the hexagonally arranged Ti-plane. The orbital order found here is consistent with

the recent predictions made by McQueen et. al.¹ on the basis of their experimental observations on a similar system NaVO₂.

Acknowledgement This work is supported by the DST (India) fast track project (grant no:SR/FTP/PS-74/2008). TM acknowledges T. Nautiyal for useful discussions. SK acknowledges CSIR (India) for a research fellowship.

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